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(54) SOLUBLE CONDENSATION PRODUCTS AND
 WATER-THINNABLE PAINT BINDERS PREPARED
 THEREFROM



(71) We, SHELL INTERNATIONALE
 RESEARCH MAATSCHAPPIJ N.V., a
 company organized under the laws of the
 Netherlands, of 30 Carel van Bylandtlaan,
 5 The Hague, the Netherlands, do hereby
 declare the invention, for which we pray that
 a patent may be granted to us, and the method
 by which it is to be performed, to be par-
 ticularly described in and by the following
 10 statement:—

Water-thinnable paint binders are usually
 prepared by composing a resin containing
 free carboxyl groups and by neutralizing the
 resin completely or partially with an alkaline
 15 material, such as a nitrogen base.

For instance, the British Patent Specifica-
 tion 962,974 discloses a process, whereby a
 20 polyglycidyl ether of a polyhydric phenol
 ("EPIKOTE" resin 1001) is completely
 esterified with linseed oil fatty acids and the
 resulting product is reacted with maleic
 25 anhydride at 240°C to introduce free car-
 boxyl groups; this maleinized resin is then
 solubilized in water by neutralization with
 ammonia and addition of ethylene glycol
 30 monobutyl ether, and used as a paint binder.
 ("Epikote" is a registered Trade Mark).

The use of water-thinnable paint binders
 35 and paints is at present well-established. One
 of the advantages is that they offer the pos-
 sibility for electro-deposition from solution
 onto metals to form a pore-free coating in
 thin layers, even at places difficult to reach
 40 with spray gun or brush, such as corners,
 nooks and pockets of a work piece.

This ability to extend the formation of
 45 electro-deposited films into difficult to reach
 places is known as the throwing power, which
 can be measured and expressed in numerical
 data, dependent on the method used. The
 throwing power depends mainly on the binder
 50 composition, and over the years that electro-
 deposition of water-thinnable paints has be-

come commercially important, much effort has
 been devoted to the developments of paint
 binders with better throwing power. At first,
 a simple test, with three metal panels clamped
 55 wedge-like together as the anode to be coated,
 was sufficiently discriminating for determin-
 ing the throwing power of different paints.
 However, with the development of better
 binders that simple test did not lend itself to
 60 detection of apparently small differences in
 throwing power of paints, which in practice
 afforded significantly different corrosion pro-
 tection, for example to automobile bodies and
 parts. Such paints can at present be discrimi-
 65 nated by a more refined throwing power test,
 the tube penetration test, wherein the spec-
 imen is a metal strip inserted in a metal tube,
 the strip and tube are supported in an elec-
 tro-deposition bath, connected as anode, and
 70 the coated length of the strip is measured.

On the other hand, the electrodeposition
 technique provides many new problems in the
 paint-binder technology. For example, paint
 driers, such as salts of cobalt and manganese,
 well-known for accelerating the cross-linking
 75 of ethylenically unsaturated fatty acid resi-
 dues of oils and resins in conventional paints
 and water-soluble paints applied by dipping,
 spraying or brushing, apparently do not have
 this function in electro-deposited films; there-
 fore hardness and other mechanical and
 chemical properties in conventional paint
 applications promoted by driers have to be
 inserted by other means, such as incorpora-
 80 tion of specific groups in the binder mole-
 cule. In the binders described in the British
 Patent Specification 962,974 one such a modi-
 fication involved the replacement of part of
 the linseed oil fatty acid by benzoic acid, to
 85 provide electro-deposited films which have
 improved hardness, and a very good corrosion
 resistance, in particular salt spray resistance,
 when formulated with chromate pigments.

[Price 25p]

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5 Chromate pigments, however, while improving the corrosion resistance of paint films, have in electro-deposition formulations the draw-back that they diminish the stability of the paint bath under conditions of continuous circulation and low paint consumption which in actual practice are often encountered. Another drawback of chromate pigments is the toxicity level which makes them not so acceptable for some applications.

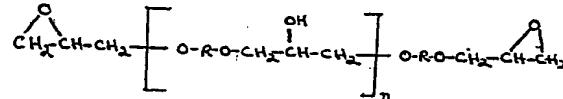
10 Other modifications of the process described in the British Patent Specification 962,974 involved the replacement of part of the linseed oil fatty acids by rosin, or a precondensation with phenolformaldehyde resins, to improve hardness of the cured film, or throwing power during electrodeposition.

15 It has now been found that a very good balance of properties can be obtained by a specific modification with carboxylated polydienes. The incorporation of these compounds is favourable for the flexibility of the ultimate cured film; further, the binders have a very good throwing power, the cured films have a good to excellent hardness, and a very good to excellent salt spray resistance, even without the use of chromate pigments.

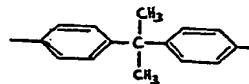
30 The invention provides a process for the preparation of soluble condensation products which contain free carboxyl groups and which are thinnable with water after neutralization, comprising (1) reacting a polyglycidyl ether of a polyhydric phenol at a temperature between 120 and 180°C simultaneously with (a) a carboxyl-containing polymer of a C₄—C₆ 1,3-diene hydrocarbon, in a ratio of from 0.02 to 0.35 acid equivalent of carboxylated polydienes per epoxy equivalent, and (b) a mono-carboxylic acid in a ratio of 0.4 to 0.98 acid equivalents per epoxy equivalent, (2) esterifying the hydroxy-containing ester with ethylenically unsaturated fatty acids in a ratio of from 0.8 to 1.3 acid equivalents of fatty acid per hydroxy equivalent of the hydroxy-containing ester at a temperature above 200°C, and (3) reacting the resultant polyester with at least 3% by weight, based on the polyester, of an ethylenically unsaturated dicarboxylic acid or an anhydride thereof.

35 40 45 50 As polyglycidyl ether of a polyhydric phenol a polyglycidyl ether of 2,2 - bis(4 - hydroxyphenyl)propane is preferred. Polyglycidyl polyethers of this type may be represented by the general formula:

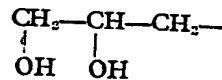
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in which R represents the divalent group:



60 and n has an average value of from 0 to, for instance, 12; during the preparation some of the terminal glycidyl groups may be hydrated to



groups by reaction with water.

65 Preferred are polyglycidyl polyethers of 2,2 - bis(4 - hydroxyphenyl)propane having a molecular weight between 340 and 1100 and an epoxy equivalent weight between 170 and 550. Particularly preferred are polyglycidyl ethers of 2,2 - bis(4 - hydroxyphenyl)propane having a molecular weight between 340 and 500 and an epoxy equivalent weight between 170 and 280.

70 The carboxylated polydienes used in step (1) may be a carboxyl-terminated liquid poly-

75 butadiene, for example, having an acid equivalent weight between 2,000 and 3,500, a molecular weight between 4,000 and 7,000, and a viscosity between 200 and 400 Poise at 25°C. A preferred carboxyl-terminated liquid polybutadiene of this type is a commercial product having an acid equivalent weight of 2590, a viscosity of 298 Poise at 25°C, in which the unsaturation is 39.3% cis, 37.2% trans, and 23.5% vinyl.

80 85 90 95 100 Other preferred carboxylated polydienes are reaction products of alpha, beta-ethylenically unsaturated dicarboxylic acids or anhydrides thereof with polymers of C₄—C₆ 1,3-diene hydrocarbons such as polybutadienes and polyisoprenes. Products of this type are known; they can be prepared by reacting, for example, maleic anhydride with the polydiene at elevated temperatures, for example between 100°C and 250°C. Preferred carboxylated dienes of this type are reaction products of maleic anhydride with liquid polybutadienes having molecular weights between 500 and 10,000; such polymers have usually a viscosity between 30 and 30,000 centipoises at 50°C, and preferably more than 50% of the double bonds are cis - 1,4 - double bonds. The reaction with maleic anhydride can be carried out by heat alone (without catalysts), or better

5 at elevated temperature in the presence of catalysts such as copper or copper compounds. Other preferred carboxylated dienes of this type are reaction products of maleic anhydride with polyisoprene, prepared for example by injecting a solution of maleic anhydride in an organic solvent into a polyisoprene rubber masticated in a mixer at temperatures between 50°C and 300°C. Maleinized polyisoprene 10 rubbers can be depolymerized by a heat treatment to products having a lower molecular weight than the original polyisoprene rubber prior to use in the present process, or else they can be used as such in the present 15 process; it is believed that some depolymerization occurs during reaction with the epoxide in the present process, as may be apparent from "regression of gelation" during the first 20 step of the present process as a result of raising the temperature (with other materials a rise in temperature on the verge of incipient gelation will usually result in progressive gelation).

25 The acid equivalent weight of the carboxylated polydiene is usually between 800 and 5,000.

30 The first step of the present process involves mainly reaction of epoxy groups of the polyglycidyl ether with carboxyl groups 35 of the components (a) and (b), as the temperature is kept between 120°C and 180°C, that means temperatures at which mainly reaction between epoxy groups and carboxyl groups occurs, and reaction between hydroxyl and carboxyl groups can be neglected. As 40 reaction of the polyglycidyl ethers with the carboxylated polydienes (which are formally polycarboxylic acids or anhydrides thereof) alone would result in highly viscous, or even 45 gelated products, the first step is performed in the presence of a monocarboxylic acid in a ratio of from 0.4 to 0.98 acid equivalents per epoxy equivalent. The excess (in acid equivalents) of monocarboxylic acid over carboxylated polydiene is instrumental for obtaining products of low viscosity, and for preventing gelation.

50 The monocarboxylic acids used in step (1) may be of all types known, for example, 55 saturated aliphatic, cycloaliphatic or aromatic monocarboxylic acids, or ethylenically unsaturated aliphatic or cycloaliphatic monocarboxylic acids. Preferred are fatty acids having from 8 to 28 carbon atoms per molecule, and mixtures thereof with rosin acids.

60 Rosin acids, also known as rosin or colophony, are largely tricyclic monocarboxylic acids, such as abietic acid and the related acids levopimaric acid, neoabietic acid, dextropimaric acid, dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid, isodextropimaric acid. Rosin acids as used in this specification also include hydrogenated rosin acids which have an enlarged content of dihydro- and tetrahydroabietic acid and hydro-

genated related acids, and disproportionated rosin acids, which by a disproportionation process contain an enlarged content of dehydroabietic acid on one hand, and an enlarged content of dihydro- and tetrahydroabietic acid on the other hand. Hydrogenation or disproportionation of rosin acids may improve colour stability of the rosin acids or of products obtained thereof.

70 It is also possible to use mixtures of unsaturated fatty acids and rosin acids known as tall oil, for example, tall oils with high rosin content or tall oils with medium rosin content.

75 The fatty acids used in step (1) are preferably ethylenically unsaturated fatty acids.

80 The reaction in step (1) may be promoted by adding catalysts, such as organic phosphines, tertiary amines, quaternary ammonium salts, and sodium carbonate.

85 The product of step (1), described as a hydroxy-containing ester, is then esterified with ethylenically unsaturated fatty acids in a ratio of from 0.8 to 1.3 acid equivalents of fatty acid per hydroxy equivalent of the hydroxy-containing ester at a temperature above 200°C, preferably between 200°C and 260°C. During this esterification water is formed by reaction of carboxyl groups of the fatty acid with hydroxyl groups of the hydroxy-containing ester. The water is removed by evaporation, for instance, by azeotropic distillation with xylene with separation of the water in a water trap. The reaction time may vary from 2 to 7 hours, dependent 90 of suitable esterification catalysts being present, such as stannous oxide, stannous octoate, sodium carbonate, calcium oxide, zinc oxide, calcium naphthenate, zinc naphthenate, zirconium salts, organic chromium compounds, tertiary amines, quaternary ammonium salts, organic phosphines, quaternary phosphonium compounds, or mixtures thereof.

95 The ethylenically unsaturated fatty acids to be used are preferably those having more than one ethylenically unsaturated group per molecule. Examples from this group of preferred fatty acids are fatty acids from drying oils such as linseed oil, tung oil, soybean oil, fish oil, cotton seed oil, oiticica oil, perilla oil, sunflower seed oil; dehydrated castor oil fatty acids and tall oil fatty acids.

100 The polyester is preferably cooled before the addition of the unsaturated carboxylic acid or carboxylic anhydride, for example, to 100—200°C.

105 The ethylenically unsaturated dicarboxylic acid, fumaric acid or maleic acid may be used; preference is given to maleic acid, which is added in the form of the anhydride. The ethylenically unsaturated dicarboxylic acid or its anhydride reacts with the completely esterified polyether mainly by addition reactions with the hydrocarbon radical of the unsaturated fatty acid groups. The reaction 110

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temperature is preferably at least 175°C, for instance, 200—250°C. With higher reaction temperatures, such as 230—250°C, the viscosity may rise considerably when using large quantities of maleic anhydride, while long reaction times may result in gelling. The maintaining of low reaction temperatures, such as 200—210°C, is favourable for obtaining low-viscosity products. In general, the reaction time is from 20 minutes to more than 1 hour. It is advisable to control the course of reaction by measuring the viscosity. The quantity of unsaturated dicarboxylic acid or its anhydride is above 3% by weight, based on the weight of the polyester. Maleic anhydride is preferably used in quantities of from 3 to 10% by weight.

The range of reactions of the polyglycidyl polyether with the other reactants is preferably carried out in an inert, oxygen-free atmosphere, for instance, by passing nitrogen through or over the reaction mixture.

The reaction product, which contains free carboxyl groups, is cooled and can immediately be neutralized or be stored and transported as such. The neutralizing agent may be an alkali metal hydroxide such as potassium hydroxide; in general a nitrogen base is preferred, such as ammonia or a primary, secondary or tertiary aliphatic or cycloaliphatic amine, for instance, triethylamine, beta-dimethyl aminoethanol, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, di-isopropanolamine, cyclohexylamine, morpholine, piperidine and piperazine. The quantity of neutralization agent is selected in such a way that at least 40% of the carboxyl groups are neutralized. The pH of the neutralized binder depends on the degree of neutralization. If all the carboxyl groups are neutralized, the pH is higher than when only 70% or 50% of the carboxyl groups are neutralized. Complete neutralization usually gives products which dissolve in water completely without any haziness; in the case of partial neutralization the solutions in water may be somewhat hazy. The adjustment to a certain pH by means of partial neutralization may be desired in connection with proper dispersion of pigments.

A lyotropic solvent, such as an ethylene glycol monoalkyl ether, for instance, ethylene glycol monobutyl ether, is preferably added to promote the clear solubility in water. Such lyotropic solvents are preferably used in quantities up to 50% by weight, based on the weight of the carboxyl-containing condensation product. In view of the rather high viscosities of the condensation products it is advisable to add the solvent or a portion thereof, for example, 10 parts by weight of lyotropic solvent per 100 parts by weight of condensation product, during the cooling of the reaction product, another amount after

cooling and then to add the neutralization agent.

The completely or partially neutralized products may be stored, if desired, thinned with water, for a long time without substantial decrease in pH and without precipitation or phase separation taking place.

The solutions of the completely or partially neutralized products may be processed with many pigments to paints in the conventional way, for instance by mixing in a ball mill, on a paint roller mill, etc. For application by spraying, brush, roller or dipping driers may be added in conventional quantities. As driers cobalt naphthenates and octoates are preferably used, for instance, in quantities up to 0.04% by weight of Co, based on the weight of the binder. Other naphthenates and octoates, such as those of zinc, calcium, manganese and lead may also be used. If desired, other curing components, such as urea formaldehyde resins and melamine formaldehyde resins, may also be added.

Paints and varnishes containing the present binders may be applied to articles in the usual way, for instance, by brush, roller or spraying. They are very suitable for electro-deposition on metals from a solution or dispersion, the metal to be coated serving as anode. The coat applied is hardened in a short time, preferably by accelerated drying at elevated temperature, such as 100—200°C.

The invention is illustrated by some Examples.

The materials used in the Examples were as follows:

Polyether A:

A liquid polyglycidyl ether of 2,2 - bis(4 - hydroxyphenyl)propane having an epoxide equivalent weight of 185 and a free hydroxyl content of 0.06 eq./100 g.

Polyether D:

A solid polyglycidyl ether of 2,2 - bis(4 - hydroxyphenyl) - propane having 0.214 epoxide equivalent and 0.252 hydroxy equivalent per 100 g.

Maleinized polyisoprene rubber:

A polyisoprene rubber, maleinized with a solution of maleic anhydride, and having an acid equivalent weight of 4,900.

Maleinized liquid polybutadiene:

A liquid polybutadiene, having a molecular weight between 1500 and 2,000, and a viscosity of about 750 cP at 20°C, heated with maleic anhydride and copper naphthenate (9% wt Cu) in a weight ratio 50:3:0.15 during 3 hours at 190°C under inert gas with stirring. The product had an acid equivalent weight of 950 (theoretical: 866).

Carboxy-terminated polybutadiene:

A liquid polybutadiene material, having an acid equivalent weight of 2590, a molecular weight of about 5200, a viscosity of 298 5 Poise at 25°C, in which the unsaturation is 39.3% cis, 37.2% trans, and 23.5% vinyl.

The throwing power was examined according to the "tube penetration test" described in Journal of Paint Technology, Vol. 38, (1966), page 454. This method can be summarized as follows: a 37.5 cm long, 1.25 cm wide strip of metal to be coated is inserted into a 1.56 cm internal diameter tube of the same material and 30 cm length. Tube and strip 10 are inserted in an electrodeposition bath, connected as anode, and coated for the desired length of time. The well-coated length of the strip is recorded.

Example 1

A. Preparation of condensation product

A 2 litre round-bottom flask equipped with anchor stirrer, thermometer, nitrogen-inlet tube, reflux condenser with water trap, and heating jacket was charged with the following materials:

Polyether A	88 g
Maleinized polyisoprene rubber	145 g
Linseed oil fatty acids	62 g
Benzylidimethylamine	1 g
30 Xylene	1,000 g

The mixture was refluxed during 8 hours (reflux temperature 140°C); the acid value was then <1 mg KOH/g.

One third of the xylene was distilled off 35 without reflux 211.6 g of linseed oil fatty acids and 1.0 g of stannous octoate were added, the major part of the remaining xylene was distilled off until the temperature was 240°C. While refluxing this temperature was 40 maintained during 5½ hours with azeotropic removal of the water formed. The acid value was then 11.1 mg KOH/g.

The polyester was cooled to 180°C, maleic anhydride (25.8 g) was added, and the mixture was heated at 200°C during 1½ hours; the acid value of the product was 60 mg KOH/g.

The condensation product was cooled to 80°C, and diluted with ethylene glycol monobutyl ether (butyl "Oxitol") to give a solids content of 84.2% by weight. ("Oxitol" is a registered Trade Mark).

B. Preparation of a pigmented water-thinnable primer

55 The pigment was a mixture of titanium dioxide (7 parts by weight), clay (1 part by weight), carbon black (0.05 parts by weight), strontium chromate (1 part by weight), basic lead silico chromate (1 part by weight), and 60 colloidal silica (0.1 part by weight).

In a ball mill the pigments were compounded with 1.2 times their weight of a 25 wt-% binder solution in water butyl "Oxitol"; (binder neutralized with 0.45 times the theoretical amount of triethyl amine); the ball mill paste was mixed with a 25 wt-% binder solution (neutralized with triethyl-amine; neutralization degree 0.45) and diluted with demineralized water to give a paint having a pigment/binder weight ratio of 0.45, a 65 solids content of 15 wt-%, and a pH of 9.0.

C. Evaluation of the primer prepared at B

The primer was electro-deposited on 75 bonderized steel panels (surface 330 cm²) in the bath during 2 minutes at a constant voltage of 165 V and a temperature of 25°C. The throwing power was 18 cm at 175 V, the rupture voltage >300 V, the film thickness 25 microns. The films were stoved at 175°C during 30 minutes; the results were:

film appearance	good
Buchholz hardness (DIN 53153)	80
Conical bend (ASTM/D522-60)	85
Erichsen impact (direct and reverse)	>90 kg×cm
Salt spray resistance 240 hours (ASTM B 117-64)	0 mm creep
Resistance to KOH (5 wt %), 23°C, 24 hours (ASTM D 714-56)	8 M
Resistance to solvents (minutes to total softening)	95
xylene	2½
methyl isobutyl ketone	2½
acetone	½

Example 2

A. Preparation of condensation product

The equipment of Example 1, A, was charged with:

Polyether D	147 g
Maleinized polyisoprene rubber	75 g
Linseed oil fatty acids	83.8 g
Benzylidimethylamine	1 g
Xylene	800 g

and heated with reflux (reflux temperature 140°C) during 7 hours; the acid value was then 1 mg KOH/g.

Linseed oil fatty acids (222.1 g) and stannous octoate (1 g) were added, and the temperature was raised to 240°C by distilling off xylene without refluxing. The temperature was kept at 240°C during 5½ hours with 115 reflux and azeotropic removal of the water formed. The acid value was then 12 mg KOH/g.

The polyester was cooled to 180°C, maleic

anhydride (27.5 g) was added, and the mixture was heated at 200°C during 1½ hours.

The condensation product was cooled to 80°C, and diluted with ethylene glycol monobutyl ether (butyl "Oxitol") to give a solids content of 80% by weight.

B. Preparation of a pigmented water-thinnable binder

The pigment was a mixture of iron oxide (12 parts by weight), titanium dioxide (7 parts by weight), and clay (1 part by weight).

In a ball mill the pigments were compounded with 1.2 times their weight of a 25 wt-% binder solution in water/butyl

15 "Oxitol": (binder neutralized with a 0.4 times the theoretical amount of triethyl amine); the ball mill paste was mixed with a 25 wt-% binder solution (neutralized with triethyl amine; neutralization degree 0.4) and diluted with demineralized water to give a

20 paint having a pigment/binder weight ratio of 0.35, a solids content of 15 wt-%, and a pH of 8.61.

C. Evaluation of the primer prepared at B

The primer was electro-deposited on bonderized steel panels (surface 330 cm²) in the bath during 2 minutes at a constant voltage of 300 V and a temperature of 25°C. The throwing power was 21 cm at 300 V, the rupture voltage >500 V, the film thickness 25 microns. The films were stoved at 175°C during 30 minutes; the results were:

	Film appearance	fair
35	Buchholz hardness	130
	Conical bend	pass
	Erichsen impact (direct and reverse)	>90 kg×cm
	Salt spray resistance (240 hours)	3—5 mm creep
40	Resistance to solvents (minutes to total softening)	
	xylene	3½
	methyl isobutyl ketone	2½
45	acetone	½

Example 3

A. Preparation of condensation product

The equipment of Example 1, A, was charged with:

50	Polyether D	147 g
	Maleinized polyisoprene rubber	35 g
	Rosin	80 g
	Linseed oil fatty acids	18 g
55	Benzylidimethylamine	1 g
	Xylene	600 g

and heated with reflux (reflux temperature 140°C) during 5½ hours; the acid value was then <1 mg KOH/g.

Linsseed oil fatty acids (225 g) and stan-

nous octoate (1 g) were then added, and the temperature was raised to 240°C by distilling off xylene without refluxing. The temperature was kept at 240°C during 4½ hours with reflux and azeotropic removal of the water formed. The acid value was then 10.3 mg KOH/g.

60 The polyester was then cooled to 180°C, maleic anhydride (22 g) was added, and the mixture was heated to 200°C during 1½ hours.

70 The condensation product was cooled to 80°C and diluted with ethylene glycol monobutyl ether (butyl "Oxitol") to give a solids content of 80% by weight.

B. Preparation of a pigmented water-thinnable binder

The pigment was a mixture of iron oxide (12 parts by weight), titanium dioxide (7 parts by weight), and clay (1 part by weight).

80 In a ball mill the pigments were compounded with 1.2 times their weight of a 25 wt-% binder solution in water/butyl "Oxitol": (binder neutralized with 0.45 times the theoretical amount of triethyl amine); the ball mill paste was diluted with a 25 wt-% binder solution (neutralized with triethyl amine; neutralization degree 0.45), and diluted with demineralized water to give a paint having a pigment/binder weight ratio of 0.4, a solids content of 15 wt-%, and a pH of 8.81.

85 **C. Evaluation of the primer prepared at B**

90 The primer was electro-deposited on bonderized steel panels (surface 330 cm²) in the bath during two minutes at a constant voltage of 120 V and a temperature of 25°C. The throwing power was 12 cm at 120 V, the rupture voltage 400 V, the film thickness 25 microns. The films were stoved at 175°C during 30 minutes; the results were:

	Film appearance	good
95	Buchholz hardness	100
	Conical bend	pass
	Erichsen impact (direct and reverse)	>90 kg×cm
	Salt spray resistance (240 hours)	2—4 mm creep
100	Resistance to solvents (minutes to total softening)	
	xylene	3½
	methyl isobutyl ketone	2½
	acetone	¾

Example 4

A. Preparation of condensation product

115 A 1 litre round-bottom flask equipped with anchor stirrer, thermometer, nitrogen-inlet tube, reflux condenser with water trap, and heating jacket was charged with the following materials:

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	Polyether A	88 g	Polyether A	88 g	
	Maleinized liquid polybutadiene	95 g	Carboxy-terminated polybutadiene	212 g	60
	Wood rosin	88 g	Linseed oil fatty acids	107 g	
	Linseed oil fatty acids	28 g	Benzylidimethylamine	0.5 g	
5	Benzylidimethylamine	1 g	Copper naphthenate	0.5 g	
	Copper naphthenate	0.5 g	Xylene	800 g	
	Water	2 g			
	Xylene	200 g			

10 The mixture was refluxed during 6 hours (reflux temperature 140—145°C); the acid value was then 1 mg KOH/g.

15 Linseed oil fatty acids (170 g) and stannous octoate (1.1 g) were added, and the xylene was distilled off until the temperature was 240°C. While refluxing this temperature was maintained during 6 hours with azeotropic removal of the water formed. The acid value was then 5 mg KOH/g.

20 The polyester was cooled to 180°C, maleic anhydride (25.5 g) was added, and the mixture was heated at 200°C during 45 minutes; the acid value of the product was 60 mg KOH/g.

25 The condensation product was cooled to 80°C and diluted with ethylene glycol monobutyl ether (butyl "Oxitol") to give a solids content of 72.8% by weight.

B. Preparation of a pigmented water-thinnable binder

30 This paint was prepared from the condensation product described at Example 4 (A) as described in Example 2 (B): the condensation product was neutralized with triethylamine (neutralization degree: 0.4), with the exception that the pigment/binder weight ratio was 0.40. The paint had a solids content of 15 wt-%, a pH of 8.9, and a specific resistance of 1120 Ω cm.

35 C. Evaluation of the primer prepared at B
40 The primer was electro-deposited on bonderized steel panels (surface 330 cm²) in the bath during 2 minutes at a constant voltage of 200 V and a temperature of 25°C. The throwing power was 20 cm at 200 V, the rupture voltage >400 V, the film thickness 25 microns. The films were stoved at 175°C during 30 minutes; the results were:

	Film appearance	good		
	Buchholz hardness	125		
50	Conical bend	pass		
	Erichsen impact (direct and reverse)	>67.5 kg×cm		
	Salt spray resistance (240 hours)	3—4 mm creep.		

55 Example 5

A. Preparation of condensation product

The equipment of Example 1, A, was charged with:

	Polyether A	88 g		
	Carboxy-terminated polybutadiene	212 g	60	
	Linseed oil fatty acids	107 g		
	Benzylidimethylamine	0.5 g		
	Copper naphthenate	0.5 g		
	Xylene	800 g		

The mixture was refluxed during 15 hours (reflux temperature 140°C); the acid value was then 1 mg KOH/g.

70 Linseed oil fatty acids (180 g) and stannous octoate (1 g) were added, and the xylene was distilled off until the temperature was 240°C. While refluxing this temperature was maintained during 5 hours with azeotropic removal of the water formed. The acid value was then 12.1 mg KOH, which indicates a 97% esterification.

75 The polyester was cooled to 190°C, maleic anhydride (27 g) was added, and the mixture was heated at 190—200°C during 90 minutes; the acid value of the product was 60 mg KOH/g.

80 The condensation product was cooled to 100°C and diluted with ethylene glycol monobutyl ether (butyl "Oxitol") to give a solids content of 72.8% by weight.

B. Preparation of a pigmented water-thinnable binder

This paint was prepared as described in Example 4, B:

neutralization with	triethyl amine	
neutralization degree	0.4	90
pigment/binder weight ratio	0.4	
solids content	15 wt-%	
pH	9.05	
specific resistance	1135 Ω cm	

C. Evaluation of the primer prepared at B

95 The primer was electro-deposited on bonderized steel panels (surface 330 cm²) in the bath during 2 minutes at a constant voltage of 200 V and a temperature of 25°C. The throwing power was 27 cm at 200 V, the rupture voltage >500 V, the film thickness 25 microns. The films were stoved at 175°C during 30 minutes; the results were:

Film appearance	good	
Buchholz hardness	80—90	105
Conical bend	pass	
Erichsen impact (direct and reverse)	>90 kg×cm	
Salt spray resistance (240 hours)	10 mm creep.	110

WHAT WE CLAIM IS:—

1. A process for the preparation of soluble condensation products which contain free carboxyl groups and which are thinnable with water after neutralization, comprising (1) reacting a polyglycidyl ether of a polyhydric phenol at a temperature between 120 and

180°C simultaneously with (a) a carboxyl-containing polymer of a C₄—C₆ 1,3-diene hydrocarbon, in a ratio of from 0.02 to 0.35 acid equivalent of carboxylated polydiene per epoxy equivalent, and (b) a monocarboxylic acid in a ratio of 0.4 to 0.98 acid equivalents per epoxy equivalent, (2) esterifying the hydroxy-containing ester with ethylenically unsaturated fatty acids in a ratio of from 0.8 to 1.3 acid equivalents of fatty acid per hydroxy equivalent of the hydroxy-containing ester at a temperature above 200°C, and (3) reacting the resultant polyester with at least 3% by weight, based on the polyester, of an ethylenically unsaturated dicarboxylic acid or an anhydride thereof.

2. A process as claimed in claim 1, wherein the polyglycidyl ether is a polyglycidyl ether of 2,2 - bis(4 - hydroxyphenyl)propane having an average molecular weight between 340 and 1100 and an epoxy equivalent weight between 170 and 550.

3. A process as claimed in claim 1 or 2, wherein the carboxylated polydiene used in step (1) is a carboxyl-terminated liquid polybutadiene.

4. A process as claimed in claim 1 or 2, wherein the carboxylated polydiene is a reaction product of a polymer of a C₄—C₆ 1,3-diene hydrocarbon with an alpha, beta-ethylenically unsaturated dicarboxylic acid or an anhydride thereof.

5. A process as claimed in claim 4, wherein the carboxylated polydiene is a reaction product of a liquid polybutadiene having an average molecular weight between 500 and 10,000 with maleic anhydride.

6. A process as claimed in claim 4, wherein the carboxylated polydiene is a reaction product of polyisoprene with maleic anhydride.

7. A process as claimed in any one of claims 1 to 6, wherein the monocarboxylic acid used in step (1) is a fatty acid having from 8 to 28 carbon atoms per molecule.

8. A process as claimed in any one of claims 1 to 6, wherein the monocarboxylic acid used in step (1) is a mixture of a fatty acid having from 8 to 28 carbon atoms per molecule, and rosin acids.

9. A process as claimed in claim 7 or 8, wherein the fatty acid used in step (1) is an ethylenically unsaturated fatty acid.

10. A process as claimed in any one of claims 1 to 9, wherein the ethylenically unsaturated fatty acids used in step (2) contain more than one ethylenically unsaturated group per molecule.

11. A process as claimed in any one of claims 1 to 10, wherein the reactions are carried out in the presence of an esterification catalyst.

12. A process as claimed in any one of claims 1 to 11, wherein as the ethylenically unsaturated dicarboxylic acid anhydride in step (3) maleic anhydride is used in an amount between 3 and 10% by weight of the polyester.

13. A process as claimed in any one of claims 1 to 12, wherein in step (3) the reaction with the ethylenically unsaturated dicarboxylic acid or anhydride thereof is carried out at a temperature of at least 175°C.

14. A process as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

15. A condensation product prepared by the process claimed in any one of claims 1 to 14.

16. A process for the preparation of a water-thinnable binder, wherein at least 40% of the free carboxyl groups of a condensation product as claimed in claim 15 are neutralized.

17. A process as claimed in claim 16, wherein the neutralization is carried out with a nitrogen base.

18. A process as claimed in claim 17, wherein the nitrogen base is a primary, secondary, or tertiary aliphatic or cycloaliphatic amine.

19. A process as claimed in claim 16 and substantially as hereinbefore described.

20. A process as claimed in any one of claims 1 to 14 and 16 to 19, wherein a lyotropically active solvent is added to the condensation product prepared according to any one of claims 1 to 10 or to the binder partly or completely neutralized according to any one of claims 16 to 19.

21. A process as claimed in claim 20, wherein the lyotropically active solvent is ethylene glycol monobutyl ether.

22. A process for the preparation of a water-thinnable binder substantially as hereinbefore described with reference to any one of Examples 1 to 5.

23. A water-thinnable binder prepared as claimed in any one of claims 16 to 22.

24. A water-thinnable paint or varnish, comprising a binder as claimed in claim 23.

25. A water-thinnable binder substantially as hereinbefore described with reference to any one of Examples 1 to 5.

26. A water-thinnable primer substantially as hereinbefore described with reference to any one of Examples 1 to 5.

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